

.. Lactoprene..

New Synthetic Rubber

Acrylic ester copolymers containing vulcanizable unsaturation were prepared by polymerizing methyl acrylate or ethyl acrylate with small quantities of polyfunctional monomers, such as butadiene, isoprene, and allyl maleate. Compounding the soft copolymers with sulfur and accelerators, followed by curing, produced rubbery

vulcanizates. Several abundant carbohydrates can be converted, through lactic acid as an intermediate, into approximately an equal weight of vulcanized acrylic resins. Because of the key role played by lactic acid in this transformation, the name "Lactoprene" is proposed for synthetic rubber of this type as described here.

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UNLIKE many polymerized methacrylic acid derivatives, polymers prepared from the *n*-alkyl acrylates (16) are soft and elastic at room temperature. The rubberlike properties of the polymerized acrylic esters have been pointed out by several workers, and the acrylic resins are actually being used as rubber substitutes for certain purposes (20, 29).

Although elastic plastics such as the acrylic and vinyl resins have many uses, it appeared that proper cross linkage or vulcanization might transform these essentially linear polymers into products more nearly resembling rubber. The method of cross linking first selected consisted in copolymerizing the lower alkyl acrylates with small proportions of a polyfunctional monomer and vulcanizing the resulting copolymer (assumed to have olefinic unsaturation) according to the technique and with the agents used in the rubber and synthetic rubber industries.

Vulcanization effected with sulfur, accelerators, and other agents used in rubber compounding, transformed the acrylic resins into rubberlike products that appear to have attractive possibilities. Although this study of vulcanized acrylic resins is not complete, the results are reported because of the unusual current interest in synthetic rubbers (9). Several normally abundant carbohydrates can be transformed, through lactic acid (27) as intermediate, into approximately an equal weight of these new rubberlike materials. Because of the key role played by lactic acid in this transition of carbohydrates into rubber substitutes, the name "Lactoprene" is proposed for vulcanized acrylic resins of the type described in this paper.

The first patent obtained by Rohm (22, 23), who pioneered the industrial exploitation of acrylic resins, was concerned with making artificial rubber. Rohm prepared his rubber substitute by mixing a polymerized acrylic ester with sulfur and "vulcanizing" the mixture at about 40° C., for 2 hours. The mechanism and nature of this vulcanization of essentially saturated acrylic polymers were not described.

Rohm and Bauer (24) described the preparation of acrylic resin mixtures, containing mineral fillers and other materials, which they claimed were suitable for the manufacture of skid-proof tires. According to the reports of other investigators (11, 13), rubberlike materials have been made by the emulsion polymerization of acrylic esters, and the rubberlike properties of acrylic resins have been enhanced by the admixture of tannic acid, ferric acetate, copper powder, and antimony potassium tartrate (25).

Nowak (17, 18, 19) claimed that vulcanization does not occur when polyacrylic esters and sulfur mixtures are heated

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unless a surface catalyst, such as carbon black, is present. His process of making rubberlike materials consisted in incorporating sulfur, β -naphthol, carbon black, and talc into polymerized ethyl acrylate

by milling at 90° to 110° C.

Vulcanization of acrylic polymers having olefinic unsaturation has been mentioned briefly. Mark and Fikentscher (15) prepared a polymer of allyl acrylate by treating polyacrylyl chloride with allyl alcohol, and stated that vulcanization transformed it into rubberlike products. The copolymers of vinyl β -methylcrotonate and an acrylic ester have been vulcanized with sulfur, presumably by virtue of unsaturation furnished by the vinyl β -methylcrotonate (12).

Butadiene and related dienes have been copolymerized with either acrylic esters (1, 6, 8, 31) or methacrylic esters (10) to form rubberlike products. Usually three parts of butadiene were used for each part of acrylic ester. The resulting copolymers would be expected to have considerable unsaturation and hence be capable of vulcanization. Regardless of the merits of this type of synthetic rubber, such products contain more butadiene than acrylic ester and therefore are more appropriately classified as butadiene rubbers.

POLYMERIZATION AND VULCANIZATION

Methyl acrylate was polymerized with small amounts of butadiene or with acrylonitrile-butadiene mixtures (Table I) in preliminary experiments to find conditions which would produce soft, rubberlike polymers. Most of these polymerizations were carried out in a bottle in an electrically heated oven. Agitation was provided by rotation of the bottle, and the temperature of the oven was controlled automatically. In experiment 9 the monomers were dissolved in ethyl acetate prior to polymerization in a three-neck flask. The polymer of experiment 10 was prepared by mass polymerization in a closed test tube. A glass vessel or liner located in an autoclave was used for some of the experiments described in Table I.

In Experiment 28 (Table II), the monomer mixture containing benzoyl peroxide (2.45%) was polymerized with stirring or kneading in a stainless-steel mixer (one-quart capacity) in the absence of solvent or dispersing medium. The mixer was fitted with an efficient reflux condenser because of the exothermic nature of the polymerization. During this mass or bulk polymerization, at reflux temperature, the monomer mixture was added in portions.

The emulsion polymerizations of Table II were carried out in round-bottom, three-neck, Pyrex flasks fitted with thermometer

Table I. Polymerization of Mixtures of Methyl Acrylate, Acrylonitrile, and Butadiene

Expt. No.	Monomers, Grams			Water, Ml.	Aerosol OT, Grams	Sodium Oleate, Grams	Rennet Casein, Grams	Other Components, Grams	Catalyst, Benzoyl Peroxide, Grams	Time, Hr.	Temp., °C.	Properties
	Methyl acrylate	Acrylonitrile	Butadiene									
1 ^a	14.25	0	0.75	60	0.5	0.5	0.5	Lecithin, 0.5	0.15	18	40	Hard and tough
2 ^a	14.25	1.0	0.75	60	0.5	0.5	0.5	Lecithin, 0.5	0.15	18	40	Elastic and strong
3 ^a	15.1	0	1.6	115.0	1.0	0.5	1.5	Gum tragacanth, 0.1; n-amyl alcohol, 0.25 ml.	0.17	Hard and tough
4 ^a	18.7	1.2	3.7	230	2.0	2.0	2.0	Lecithin, 2	0.19	18	50	Hard and dark
5 ^a	19.5	2.2	2.3	230	2.0	2.0	2.0	Lecithin, 2	0.2	18	60	Hard and tough
6 ^a	60.2	8.0	4.8	240	2.0	2.0	2.0	Lecithin, 2	0.6	18	45	Rubbery
7 ^a	60.2	16.0	4.8	240	2.0	2.0	2.0	Lecithin, 2	0.6	18	45	Hard, tough, amber-colored
8 ^a	45.0	2.5	2.5	210	2.0	2.0	1.0	Starch derivative, 2.0 ^b	0.22	22	40	Rubbery
9 ^c	31.5	1.75	1.75	Ethyl acetate, 140 ml.	0.15	Rubbery; good retraction
10 ^d	9.0	0.5	0.5	0.04	24	55	Very rubbery
11 ^a	55	1.5	3.0	210	2.0	2.0	1.0	Starch derivative, 2.0 ^b	0.3	Rubbery
12 ^a	45	1.5	5.0	180	1.5	1.5	0.5	..	60	Extremely rubbery; bounced
13 ^a	100	10	25	470	4.0	4.0	4.0	..	1.05	24	55	Tough; not rubbery
14 ^a	60	0	22.2	310	2.0	2.0	2.0	..	0.6	22	68	Hard and tough
15 ^a	43	2.0	14.4	230	1.5	1.5	0.52	20	80	Soft and rubbery
16 ^a	40	0	6.0	130	1.0	1.0	1.0	..	0.8	9	85	Soft and rubbery
17 ^a	40	2	6	130	1.0	1.0	1.0	..	0.8	2	85	Soft and granular
18 ^a	62	3	59.5	425	2.5	2.5	2.5	..	1.9	5	75-107	Soft and granular

^a Polymerized in rotating bottle located in oven.

^b Product prepared from starch and chloroethyl ether by S. G. Morris of this Laboratory.

^c Solution polymerized, with stirring, in a three-neck flask.

^d Polymerized in a sealed tube.

^e Polymerized in a glass-lined rotating bomb.

well, reflux condenser, and water-sealed stirrer (ground-glass joints). The stirrers were paddle, anchor, or half-moon type and were rotated at 75 to 150 r.p.m. The monomer mixture was added to the water and emulsifier (Triton K60S, solution of cetyl dimethyl benzyl ammonium chloride, 30) in the flask, stirred, and heated to refluxing temperature. The desired amount of catalyst was then added, either all at once or in several portions. If necessary, heating was applied to maintain gentle refluxing, and the course of the polymerization was followed by noting changes in the refluxing temperature. When refluxing ceased in spite of heating (usually about 92° C.), the polymerization was considered finished. The emulsion was then removed from the flask, coagulated with a dilute solution of sodium chloride, washed with water, and air-dried.

The compounding ingredients (Table III) were milled into the polymers on a miniature compounding mill which had steam-heated, 4 × 8 inch rolls. As compared with other synthetics, most of the polymers were easily milled and required little or no breakdown before forming a rolling bank. Even when 60 parts of carbon black per 100 parts of polymer were used, the mixture could be milled without undue difficulty. Several of the samples had a tendency to adhere to the back roll. The milling time was short and approximately equal to that required for natural rubber.

The compounded mixtures were cured in stainless-steel "sandwich" molds to obtain sheets having the dimensions 4 × 4 × 0.025 inch. In the initial stages of the study, the cured specimens adhered to the sandwich and removal from the mold was difficult. The method of curing the specimens between two sheets of cellophane was then adopted and used in the later experiments.

In most instances the polymers were compounded according to a Butyl rubber formula. The following ingredients were used (parts per 100 parts of polymer): Captax (mercaptobenzothiazole), 0.5; zinc oxide, 5; stearic acid, 2; sulfur, 2; Furnex Beads (carbon black), 30; Tuads (tetramethylthiuram disulfide) 1. The

compounded mixtures were cured under various conditions, but only the conditions leading to best results are reported in Table III. The best compounding formula and optimum curing conditions were not determined.

The tensile strength, ultimate elongation, and hardness (Shore A durometer) were determined by standard methods, except that the specimen was not of standard thickness. The behavior of some of the samples in a hydrocarbon solvent (50% toluene-50% heptane) was determined by immersing a weighed specimen in the solvent for periods of 1 to 4 days, allowing it to dry for 30 minutes, and then weighing. The results are given in Table III. The brittle points of some of the samples were determined with apparatus of the type described by Selker, Winspear, and Kemp (14, 26). The bath liquid was petroleum ether. Specific gravity was determined by suspending the sample in standard zinc chloride solutions, according to a previously described method (2). The specific gravity of the samples examined was approximately 1.31. Natural rubber, Neoprene GN, Buna S, Thiokol F, Koro-

Table II. Polymerization of Acrylic Esters in the Presence of Polyfunctional Monomers

Expt. No.	Monomers, Grams	Water, Ml.	Triton K60S, Grams	Time, Min.	Catalyst, Ml. ^a
19	Ethyl acrylate, 90; allyl lactate maleate, 10	150	2.0	60	H ₂ O ₂ , 1
20	Ethyl acrylate, 180; allyl lactate maleate, 20	250	3.0	55	H ₂ O ₂ , 1
21	n-Butyl acrylate, 60; allyl lactate maleate, 20; methyl acrylate, 120	250	3.0	80	H ₂ O ₂ , 1
22	Ethyl acrylate, 500; allyl maleate, 55	700	8.5	30	H ₂ O ₂ , 5.5
23	Methyl acrylate, 85; 2-ethyl hexyl acrylate, 10; allyl maleate, 5	150	2.0	60	H ₂ O ₂ , 2
24	Ethyl acrylate, 98; isoprene, 2	150	2.0	210	H ₂ O ₂ , 14; benzoyl peroxide, 2 g.
25	Ethyl acrylate, 250	300	4.0	20	H ₂ O ₂ , 0.5
26	Ethyl acrylate, 99.5; allyl maleate, 5	150	2.0	45	H ₂ O ₂ , 0.5
27	Ethyl acrylate, 98; allyl maleate, 2	150	2.0	55	H ₂ O ₂ , 0.5
28 ^b	Ethyl acrylate, 380; isoprene, 20	130	Benzoyl peroxide, 10 g.
29	Methyl acrylate, 140; n-butyl acrylate, 42; allyl lactate maleate, 20	275	3.0	..	H ₂ O ₂ , 4
30	Methyl acrylate, 46.5; n-butyl acrylate, 46.5; allyl lactate maleate, 12	150	2.0	..	H ₂ O ₂ , 2; benzoyl peroxide, 0.5 g.
31	Methyl acrylate, 70; acrylonitrile, 3; butadiene, 13.5	250	..	26 hr.	Benzoyl peroxide, 0.7 g.
32	Ethyl acrylate, 90; acrylonitrile, 5; allyl maleate, 5	150	2	6.75 hr.	H ₂ O ₂ , 3.5
33	Ethyl acrylate, 95; allyl maleate, 5	150	2	40	H ₂ O ₂ , 2 ^d
34	Ethyl acrylate, 180; acrylonitrile, 10; allyl maleate, 10	250	2	65	H ₂ O ₂ , 2.5 ^e

^a The concentration of hydrogen peroxide was 30%.

^b Mass polymerization.

^c Emulsifying agents were 2 grams Aerosol OT, 2 grams sodium oleate, and 2 grams casein.

^d Mercaptan 3B (0.5 ml.) also was present during the emulsion polymerization.

^e Dodecyl mercaptan (0.5 ml.) also was present during the emulsion polymerization.

Table III. Vulcanization and Test Data^a

Expt. No.	Deviations from Standard Formula, Parts	Curing Conditions		Tensile Strength, Lb./Sq. In.	Ultimate Elongation, %	Shore A Hardness	% Gain in Wt. after Immersion in		Brittle Point, ° C.
		Min.	° F.				50 toluene, 50 heptane	Water	
19	2 Tuads	180	274	290 ^b	800	35
20A	20 Furnex Beads	120	274	270 ^b	210	48
20B	Furnex Beads omitted	150	274	190 ^b	300	35
20C	30 Micronex in addition to Furnex	90	274	890 ^b	140	77	-16
21A	40 Furnex Beads	120	274	830	160	77	12.5 ^c	4.1	-11
21B	None	150	274	820 ^b	260	63	15.5	4.9
22	40 Furnex Beads	140	294	360 ^b	300	48
23	None	30	298	1070 ^b	270	78
24	None	80	298	350 ^b	1020	50	22.0 ^c
25A	None	80	298	290 ^b	>2700	47
25B	Only 95 polymer and 5 S	360	122
25C	10 allyl lactate, maleate	80	298	0	>2800	32
26	None	80	298	340 ^b	380	48	8.5
27	None	80	298	510 ^b	700	41	20.0	1.6
28	None	110	298	440 ^b	160	50
29	2 Tuads	15	287	960	500	-6
30	3 S; 15 Furnex Beads	10	307	270	160	55
31	2 Tuads	120	274	1840 ^b	120	77	15.0
32	None	120	298	990 ^b	490	47	17.3 ^c	3.5	-8
33	None	120	298	380 ^b	530	46	16.3 ^c	3.5	-19
34	None	120	298	760 ^b	960	48	14.2	5.8	-11

^a Standard compounding formula (parts by weight): Polymer, 100; Captax, 0.5; stearic acid, 2; zinc oxide, 5; sulfur, 2; Furnex Beads, 30; Tuads, 1.

^b Apparently optimum curing conditions for maximum tensile strength were not reached.

^c Samples were weakened. ^d Polymer dissolved. ^e Vulcanization did not occur.

seal, and Hycar OR have densities of 0.92, 1.24, 0.96, 1.38, 1.33, and 1.00, respectively (?).

The *n*-butyl acrylate (21), 2-ethyl hexyl acrylate, allyl maleate, and "allyl lactate maleate" used in some of the experiments were prepared in connection with other investigations. The *n*-butyl and 2-ethyl hexyl acrylates were prepared by alcoholysis (21) of methyl acrylate. Allyl maleate was prepared by direct esterification. The allyl lactate maleate, which was made by the interaction of allyl lactate and maleic anhydride, is believed to consist mainly of di-(1-carboalloxy ethyl) maleate. Commercial grades of butadiene and isoprene (95%) were used after purification.

Several of the copolymers were insoluble in organic solvents and, hence, were probably cross linked. Presumably cross linkage was not extensive enough to preclude the presence of olefinic linkages. Probably the copolymers had olefinic unsaturation and were transformed into thermosetting products through genuine sulfur vulcanization. It should be pointed out, however, that the only evidence supporting this view is the fact that treatment with sulfur and suitable accelerators effected changes in the physical properties that roughly resembled those occurring with rubber or Butyl rubber under similar conditions.

DISCUSSION OF RESULTS

The preliminary polymerization experiments showed that soft, elastic polymers could be made from methyl acrylate and butadiene under certain conditions (Table I). With the exception of experiment 16, a tough or hard polymer was obtained when methyl acrylate and butadiene were polymerized in the absence of acrylonitrile. Probably cross linkage was responsible for the fact that these polymers were not rubberlike.

Ethyl acrylate was used in several of the experiments listed in Table II because the polymers of this ester are unusually similar to rubber in appearance and feel. Mixtures of methyl acrylate with other alkyl acrylates (*n*-butyl or 2-ethyl hexyl) were polymerized because the copolymers thus prepared were softer than the methyl acrylate polymers obtained under the same conditions. The relatively hard and tough methyl acrylate polymers could be softened by plasticization, but soft copolymers were selected for study in preference to plasticized methyl acrylate polymers.

In view of claims made by earlier workers (17, 18, 19, 22, 23, 24), attempts were made to vulcanize the polymer of ethyl acrylate (Table II, experiment 25). No effect that could be attrib-

uted to vulcanization was observed when mixtures of ethyl acrylate polymer containing sulfur alone or sulfur, carbon black, and other agents (Table III, experiment 25A and 25B) were heated under curing conditions. These results were expected, since the polymers of alkyl acrylates have little or no unsaturation.

In preparing the copolymers listed in Table II, only small amounts of the polyfunctional monomers (2 to 13.5% of the total monomer mixture) were used because the primary purpose of the copolymerization was to furnish olefinic linkages in the polymer chains. Acrylonitrile was used because it had appeared to inhibit cross linkage during the polymerization of butadiene-methyl acrylate mixtures in the preliminary experiments (Table I). Dodecyl mercaptan was used also in some experiments to prevent or retard cross linkage. The polymerization appeared to proceed smoothly and with less violence when dodecyl mercaptan was present. Possibly xanthogen disulfides, carbon tetrachloride, and other agents (?) could

be used for the same purpose.

Unlike the simple alkyl acrylate polymers (Table II, experiment 25), the unsaturated copolymers were readily vulcanized when compounded suitably with sulfur, carbon black, and certain active accelerators sometimes used with Butyl rubber (Table III). Relatively inactive accelerators were less suitable. The vulcanized samples were rubberlike in appearance and feel, and were distinctly superior to the unvulcanized products. Before vulcanization, the samples could be drawn out almost indefinitely and had negligible tensile strength. The vulcanized samples had tensile strength as high as 1840 pounds per square inch, and the elongation ranged in most instances from 200 to 800%. Shore A durometer hardness ranged from 32 to 78 (Table III). As little as 2% of the polyfunctional monomer (Table II, experiments 24 and 27) provided enough unsaturation for vulcanization.

Results obtained with an ethyl acrylate polymer plasticized with allyl lactate maleate (Table III, experiment 25C) indicate that the vulcanizable products were true copolymers. The ethyl acrylate-allyl lactate maleate copolymer (experiments 19 and 20) was vulcanizable, whereas the ethyl acrylate polymer plasticized with allyl lactate maleate could not be vulcanized under comparable curing conditions (Table III, 25C).

Although the ethyl acrylate polymer was soluble in a mixture of toluene and heptane (equal portions), the vulcanized products were insoluble in this mixture. The vulcanized products, however, swelled and absorbed some of the hydrocarbon mixture during immersion tests (Table III). Some of the products tested (21A, 21B, and 24) were noticeably weakened by immersion in the toluene-heptane mixture. The vulcanized products increased in weight as much as 5.8% when immersed in water, but no other effect was apparent.

Brittle temperatures of the samples tested (Table III) ranged from -6° to -19° C. According to Trommsdorff (28), the polymers of methyl, ethyl, and *n*-butyl acrylate have softening points of +8°, -20°, and -40° C.

POSSIBLE USES AND SOURCES

Although vulcanized acrylic resins in their present stage of development are not suitable substitutes for rubber for all purposes, it is expected that Lactoprene will prove useful as an elastomer in several fields (9). Moreover, it seems reasonable to expect that further research will improve the rubberlike properties of vulcanized acrylic resins and extend the scope of their usefulness. Even

in the present stage of development, Lactoprene is superior in tensile strength and ultimate elongation to some of the products (4, 5) now being used to replace rubber. On the basis of the results shown in Table III and the structure of vulcanized acrylic resins, Lactoprene would be expected to resist oils and aging better than natural rubber. Fisher (9) listed several fields in which oil-resistant synthetic rubbers, but not natural rubber, can be used.

POSSIBLE USES AND SOURCES

Although acrylic esters can be made from either coal or petroleum, carbohydrates merit consideration as a starting material because of their abundance in normal times, low cost, and reproducibility. Carbohydrates can be converted to acrylic esters by the following steps (27): fermentative production of lactic acid, esterification of lactic acid with methanol, acetylation of methyl lactate, and pyrolysis of the acetylated methyl lactate (3). Yields are high; one pound of carbohydrate can be transformed into approximately one pound of Lactoprene.

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